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Kinetic Study of the Reaction between Uranium Monocarbide and Water Vapor

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The rate of the reaction between uranium monocarbide and water vapor was investigated in a flow system under the conditions of 53—90°C and 20—120 mmHg. The rate of evolution and the composition of gases were measured by means of a gas chromatograph. The reaction *versus* time curve was sigmoid-shaped and found to be divided into three parts. Avrami's equation for nucleation and growth fit the first part. The second part was expressed by a quasi first order reaction. Rate constants for the first and the second parts were found to depend on the water vapor pressure, obeying Langmuir's adsorption isotherm. The activation energy for reaction and the heat of adsorption for the first part were determined to be 13.0 and 3.9 kcal/mol respectively.

The reaction of uranium monocarbide with water and other aqueous systems has been reported by many authors.[1–6] Their studies were mainly on the composition and the quantity of produced gases. Murbach[7] reported the rate of reaction between uranium monocarbide and water vapor at 20 mmHg. Albrecht and Koehl[8] studied the kinetics of the reaction between massive uranium dicarbide and water vapor at 29±3 mmHg from 50 to 200°C by a gravimeteric method. The linear rate law was followed and the activation energy was estimated at 8.35±0.7 kcal/mol.

Besson, Moreau and Phillipot[9] carried out the kinetic study of the reaction between massive uranium monocarbide and water vapor under the conditions of 1000—1200°C and 5—60 mmHg. They found that the growth of the outer layer of uranium dioxide obeyed a linear rate law, and the growth of the inner one, consisting of uranium dioxide and carbon, obeyed a parabolic rate law. The linear rate constant k was expressed as a function of water vapor pressure in the form of $k=ap/(1+bp)$, and the parabolic rate constant k' was in the form of $k'=cp^{1/6}$. The energies of activation were 8 and 55 kcal/mol respectively.

Colby[10] studied the reaction in water and water-2-propanol mixture. He found that the reaction rate was proportional to the square root of water concentration in the solution. The activation energy was estimated at 17.6 kcal/mol.

The purpose of this investigation is to obtain the quantitative data of the rate of the reaction and to find a clue to elucidate the kinetics and the

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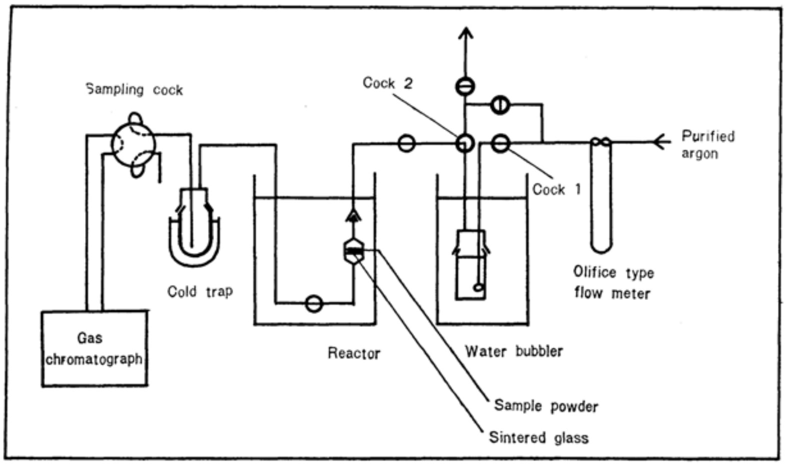

Fig. 1. The apparatus.

mechanism of the reaction between uranium monocarbide and water vapor.

Experimental

Sample. Uranium monocarbide sample was supplied from Mitsubishi Atomic Power Industries Inc., Japan. The sample was prepared as follows. The powder mixture of uranium dioxide and graphite was heated in vacuum of 10^{-4} mmHg at 1900—2000°C for 2 hr. The carburized mixture was ground to powder, from which pellets were formed by pressing. The pellets were sintered in vacuum of 10^{-4} mmHg at 2000°C. After sintering they were crushed into powder again, which was sieved to confine their particle size between 200—325 mesh. The powder was stored and handled in a glove box filled with purified argon. Analysis of the sample is given below.

Found: Total carbon, 4.65 wt%: Free carbon, 0.01 wt%: Fe, 5 ppm: Si, 10 ppm: B, 0.2 ppm: O_2, 0.21 wt%: N_2, 0.0019 wt%

Only uranium monocarbide phase was recognized by X-ray diffraction. The atomic ratio of C to U was 0.97.

Experimental Procedure. The reaction rate was determined by measuring the rate of evolution of gases in a flow system by means of a gas chromatograph. The measurement was made at the temperatures of 53—90°C under the vapor pressure of 20—120 mmHg. The apparatus is presented in Fig. 1.

Purified argon was introduced to the system after passing through a bubbler filled with water in a thermostat to be saturated with water vapor. The water was deaerated by flushing argon for about five hours prior to the reaction. The flow rate of argon was adjusted in the region of 10—200 m*l*/min by means of an olifice type flow meter. Then argon saturated with water vapor passed through a glass reaction tube (20 mm inner diameter), in which the sample was placed. The temperature of thermostats for the reactor and for the water bubbler was controlled within ±0.1°C by means of mercury regulators. The consumption of water vapor within the reactor was less than 10%. After passing through the reactor, water vapor in the gas was removed by a cold trap of dry ice-ethanol bath. A specially prepared stop cock was employed for sampling. Gas samples were analyzed by means of a gas chrmatograph with a thermal conductivity detector, using a column of molecular sieve 13 X, and argon carrier. The flow rate of the carrier gas was 23.2 m*l*/min, and the column temperature was 35°C. The measurement was started by operating the cocks 1 and 2. The reaction rate or the rate of gas evolution v, (m*l*, STP/min·g-sample), was calculated by the equation,

$$V = (PR/760)\cdot(t/273)\cdot(1/S) \tag{1}$$

where P (mmHg) is the partial pressure of gaseous products obtained from the gas chromatographic data, R (m*l*/min) is the flow rate of carrier gas, t (°K) is the temperature, and S (g) is the quantity of the sample powder. The time-lag due to the dead volume between the reactor and the sampling cock was corrected, using the flow rate of argon.

When a large quantity of sample was charged in the reactor, the measured rate constants were found to scatter widely owing to the heat of reaction. In order to eliminate this self-heating effect, a relatively small quantity (about 100—600 mg) of the sample was employed.

Results and Discussion

Products of the Reaction. Under the condition of 80.0°C and water vapor pressure 50 mmHg the reaction was carried out and interrupted halfway. The volume of evolved methane and hydrogen were obtained by measuring the rates, and other hydrocarbons by a gas chromatographic method which is reported later. The mixture of unchanged carbide and oxide produced was dissolved in 3 : 5 HNO_3, and evolved hydrocarbons were converted to carbon dioxide by combustion in oxygen stream. The weight of carbon dioxide was measured as unchanged carbon. The quantity of free carbon was also obtained by combustion

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10) L. J. Colby, USAEC Rept. NAA-SR-11401 (July 25, 1965).

TABLE 1. THE CARBON BALANCE OF THE REACTION BETWEEN URANIUM MONOCARBIDE AND WATER VAPOR OBTAINED IN THE REACTION OF 80°C, 50 mmHg

	STP volume	The quantity of carbon
CH_4	64.7 ml/g	34.7 mg/g (UC)
C_2H_6	1.52	1.63
C_3H_8	0.23	0.38
C_3H_6	0.11	0.18
i-C_4H_{10}	0.00_4	0.00_9
n-C_4H_{10}	0.07_3	0.16
1-C_4H_8	0.04_0	0.08
Free carbon		0.2
Unreacted carbon		4.6
Total		41.9

method. The carbon balance is shown in Table 1.

The starting material involves 46.5 mg/g(UC) of carbon. Accordingly, the unaccounted carbon amounts to 4.6 mg/g UC. When unreacted carbide was dissolved in nitric acid, a part of carbon would convert to mellitic acid and others.[11] A small quantity of higher hydrocarbons and waxes would be produced in the UC-H_2O vapor reaction. Unaccounted carbon is considered to consist of them. The carbon content of methane amounts to 83% of reacted carbon.

Kinetics of the Reaction between Uranium Monocarbide and Water vapor. Since the uranous oxide (IV) is produced,[12] the reaction between uranium monocarbide and water vapor is considered to proceed as follows;

$$UC + 2H_2O \rightarrow UO_2 + CH_4$$

$$UC + 2H_2O \rightarrow$$
$$UO_2 + H_2 + \text{Higher hydrocarbons}$$

$$UC + 2H_2O \rightarrow UO_2 + 2H_2 + C$$

$$U(\text{excess}) + 2H_2O \rightarrow UO_2 + 2H_2$$

The volume of hydrogen amounted to about one or two tenths of methane. As seen from Fig. 8, the ratios of hydrogen to methane in the evolved gases did not very widely during the reaction. Therefore hydrocarbons other than methane and free carbons which are accompanied with hydrogen are considered to evolve approximately in constant ratios to methane. From these results, the reaction rate would be determined by measuring only the methane evolution.

A typical curve of methane evolution is shown in Fig. 2. It is sigmoid in shape. The initial part of the curve were found to fit the Avrami's equation[13]

$$\{-\log(1-\alpha)\}^{1/n} = k_1 t \qquad (2)$$

where α and t are fractional reaction and time of reaction respectively, k_1 the rate constant and n constant. Avrami's equation had been derived from the kinetic theory of nucleation and growth,

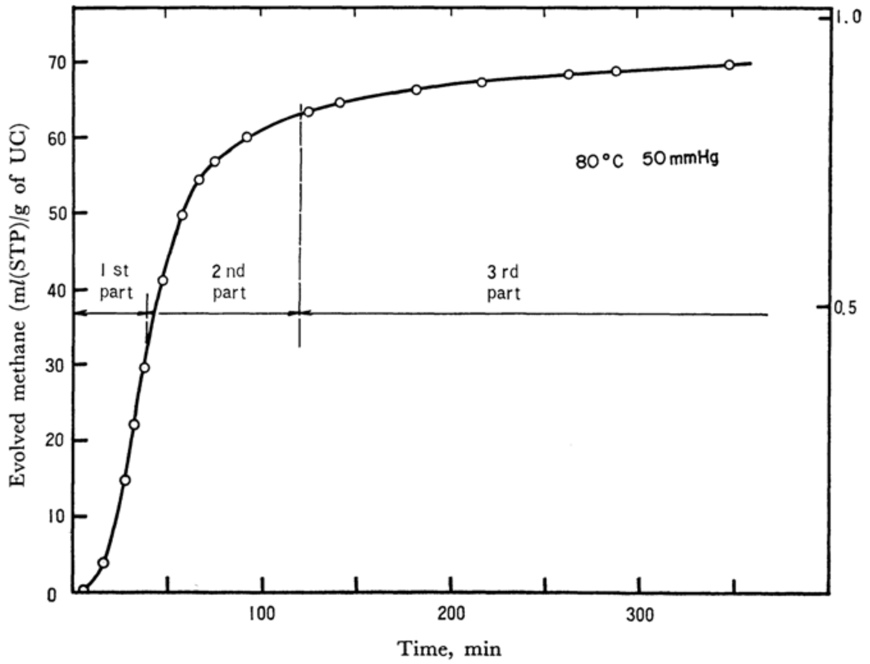

Fig. 2. A typical curve of methane evolution.

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[11] L. M. Ferris, USAEC Rept. ORNL-TM-403 (Feb. 7, 1963).

[12] Y. Hori and T. Mukaibo, *J. Nuclear Sci. Tech.*, in press.

[13] M. Avrami, *J. Chem. Phys.*, **9**, 177 (1941).

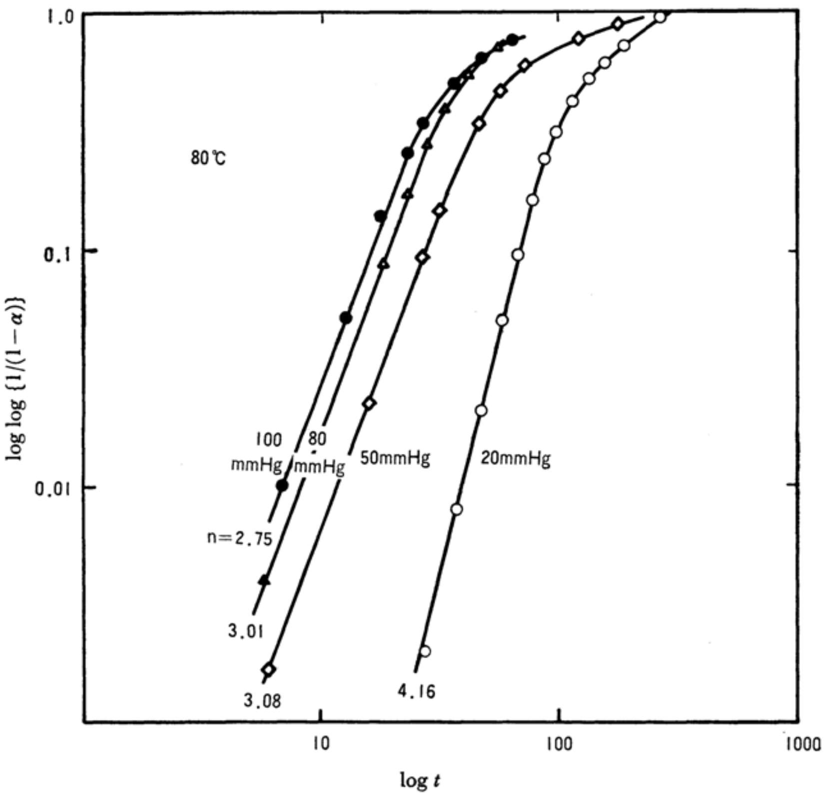

Fig. 3. A representative plot of log log $\{1/(1-\alpha)\}$ *vs.* log t

and found to be obeyed by many thermal decomposition and phase transformation processes.[14]

If the total STP volume of the evolved methane per gram of sample by the end of the reaction is represented by V, the fractional reaction is written as follows;

$$\alpha = V_{\mathrm{CH_4}}/V \tag{3}$$

where $V_{\mathrm{CH_4}}$ is the volume of methane evolved by a time t. V was found to amount to 73—78 ml/g UC in the various conditions of reaction. Representative plots of log $\{1/(1-\alpha)\}$ *versus* log t are shown in Fig. 3. The range over which Eq. (2) holds was found to be $0.0<\alpha<0.35$ above 70°C and $0.0<\alpha<0.16$ at lower temperatures with n=2—4 in both cases. The rate constants k' obtained from plots of loglog $\{1/(1-\alpha)\}$ *versus* log t, were found to depend on $P_{\mathrm{H_2O}}$, obeying the Langmuir's adsorption isotherm. Langmuir plots are shown in Fig. 4. Thus k_1 can be written as follows;

$$k_1 = C\cdot abP_{\mathrm{H_2O}}/(1+aP_{\mathrm{H_2O}}) \tag{4}$$

where C denotes the rate constant of the reaction, and a and b are the Langmuir adsorption constants.

Now $b\cdot C$ is determined from the intercept on the ordinate of plots for each reaction temperature,

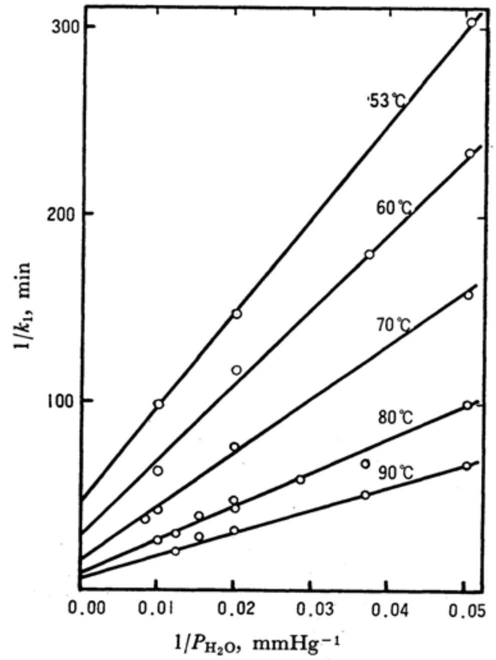

Fig. 4. Langmuir plots of the rate constants k_1.

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[14] W. G. Burgers and L. J. Groen, *Discussions Faraday Soc.*, No. 23, p. 183 (1957). P. W. M. Jacobs and A. R. T. Kureishy, "Reactivity of Solids," ed. by J. H. De Boer, Elsevier (1961), p. 352.

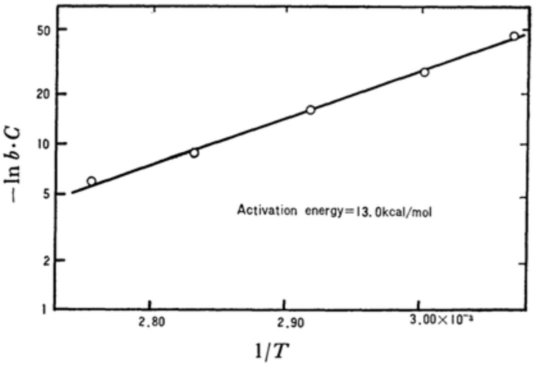

Fig. 5a. Arrhenius plot of $b\cdot C$.

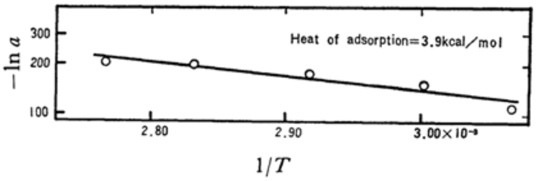

Fig. 5b. Temperature dependence of a.

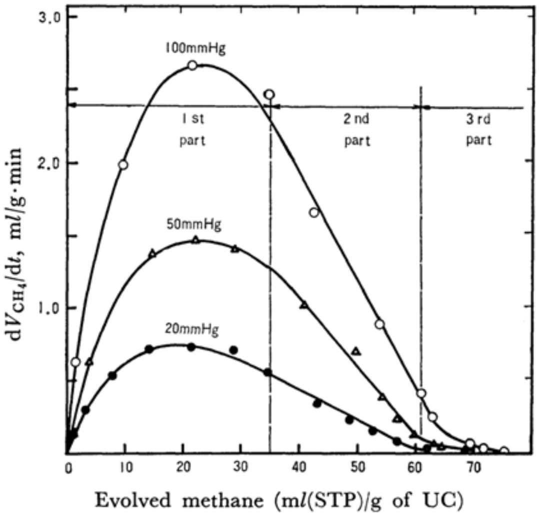

Fig. 6. The plots of the rates of methane evolution *vs.* the volume of evolved methane.

and similarly a is calculated from the slope. Usually b is regarded as the number of adsorption sites. Accordingly, if b is assumed to be constant, the activation energy for the reaction can be estimated from the Arrhenius plot of $b\cdot C$ which is shown in Fig. 5a. The activation energy is 13.0 kcal/mol. The temperature dependence of a gives 3.9 kcal/mol as the heat of adsorption (Fig. 5b).

It is apparent from Fig. 3 that the data deviate from the Avrami's equation above the fractional reaction of 0.4. The plots of dV_{CH_4}/dt *versus* V_{CH_4} are shown in Fig. 6. In the second part, the rate of methane evolution decreases linearly with the increase in the volume of evolved methane. Accordingly, the reaction rate in the second part is represented by the equation of the quasi-first order reaction;

$$dV_{CH_4}/dt = k_2(V^0 - V_{CH_4}) \tag{5}$$

where V^0 is given by the extrapolation of the linear part to the abscissa. This equation holds over the range of $0.40<\alpha<0.85$ above 70°C, and $0.30<\alpha<0.60$ at lower tempeartures (53°C and 60°C). Langmuir plots of k_2 are presented in Fig. 7. The Arrhenius plot for the constants k_2, however, not straight.

In the third part the evolution rate of methane decreased gradually, while the evolution ratio of H_2 to CH_4 increased as shown in Fig. 8.

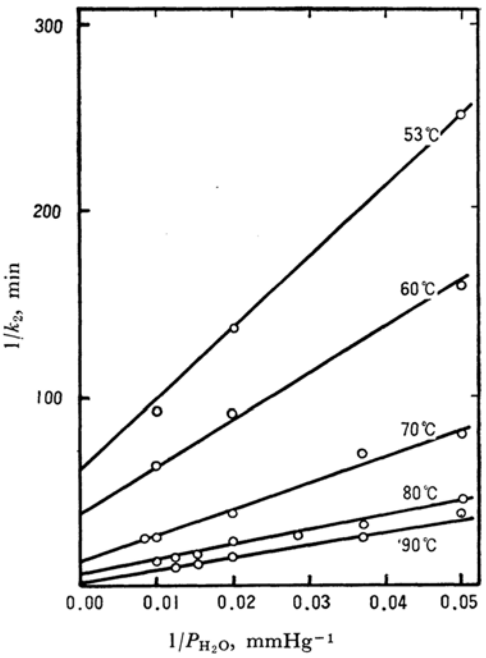

Fig. 7. Langmuir plots of the rate constants k_2.

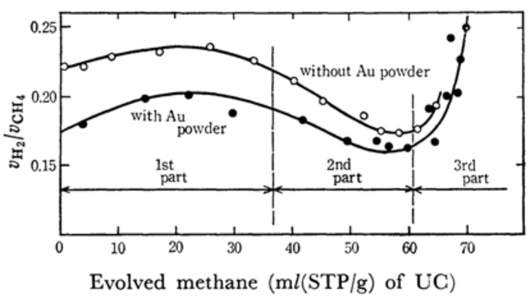

Fig. 8. The evolution ratio of H_2 to CH_4 *vs.* the volume of evolved methane.

The Rate Determining Step in the Reaction. When the reaction was completed, the apparent volume of the product was observed visually to be about ten times larger than that of carbide. Since the densities of uranium carbide and uranium dioxide are 13.63 g/cm[15] and 10.95 g/cm^3 [16] respectively, the product would consist of porous uranium dioxide. Thus the gaseous reactant and products would easily diffuse through the pores, so that the reaction could proceed.

When two kinds of gases, A & B, diffuse oppositely through a cappillery in an isobaric condition, the binary diffusion constant D_{AB} is known to depend on temperature as below;[17]

$$D_{AB} \propto T^n$$

where n is 2.334 for a binary system of water and a nonpolar gas. A plot of $\ln D_{AB}$ against $1/T$ gives a curve rather than a straight line, however, the apparent "activation energy" for the process of pore diffusion at a temperature can be obtained from the slope. The value is roughly estimated at 1.6 kcal/mol at 80°C.

As mentioned above, the activation energy obtained from the Arrhenius plot (Fig. 5a) is 13.0 kcal/mol, which is too large for pore diffusion. Consequently, the rate determining step is concluded to be the surface reaction.

A Model for Reaction Mechanism. When the Avrami's equation (2) is applied to thermal decomposition and phase transition processes, the rate constant k_1 is written as the product of the rate of nucleation N and the rate of growth of nuclei G^{n-1} for $n-1$ dimensional growth;

$$k_1{}^n = \sigma N G^{n-1} \tag{6}$$

where σ is the shape factor and G is the linear growth rate of nuclei. Thus the rate constant k_1 should be taken as the geometrical mean of N and G. However, it is still left as a problem whether or not in the first part of Fig. 2 the reaction proceeds through the process of nucleation and growth of product phase such as uranium dioxide.

According to Langmuir expression for the concentration of water molecule adsorbed on carbide,

$$[H_2O]_{ads} = abP_{H_2O}/(1+aP_{H_2O})$$

Eq. (4) can be rewritten

$$k_1 = C\cdot[H_2O]_{ads}$$

Therefore it is concluded that the adsorbed water molecules are in equilibrium with gaseous water and the rate determining step is the elementary reaction between *one* adsorbed water molecule and uranium monocarbide.

In the second part, the equation of the quasi-first order reaction was obeyed. This would be explained as follows. Owing to the expansion of the oxide, the interface of carbide and oxide may tend to collapse before the reaction is completed. Then small isolated blocks of unreacted carbide are left in oxide. For such a fine-grained particles, there is a very large surface area available for heterogeneous reaction. Once such a fine particle begins to react, it would be exhausted instantaneously. Consequently the rate of the reaction would be proportional to the amount of carbide remaining.

The Variation of the Ratio of H_2 to CH_4. In the present investigation, the ratio of H_2 to CH_4, v_{H_2}/v_{CH_4}, in the evolved gas during reaction was found to vary with the time of reaction. The preliminary experiments showed that the ratio of H_2 to CH_4 became larger as the reaction temperature became higher. To investigate whether or not the variation is owing to the self-heating effect, an experiment was carried out on a sample mixed with gold powder.*1 The uranium monocarbide sample was mixed with 300 mesh gold powder in a ratio of one to ten in weight and the reaction was carried out under the condition of 80°C and $P_{H_2O}=50$ mmHg. The result is shown in Fig. 8. The figure clearly shows that the result with gold powder is the same as that without gold powder. The variation of ratio of H_2 to CH_4 would be characteristic to the reaction.

Conclusion

1) Under the experimental conditions (53—90°C and $P_{H_2O}=20$—120 mmHg) the rate determining step was inferred to be surface reaction.

2) The curve of reaction *versus* time could be divided into three parts. The first part was expressed by Avrami's equation and the second one by the quasi-first order reaction. In the third part the gradual decrease of reaction rate was observed.

3) For the first and the second parts, the dependence of the rate constants on water vapor pressure was found to fit Langmuir's adsorption isotherm.

4) The activation energy for the reaction was estimated at 13.0 kcal/mol, and the heat of adsorption 3.9 kcal/mol for the first part.

5) The ratio of H_2 to CH_4 was observed to change during the reaction, and it is considered to be characteristic to this reaction.

The authors wish to thank Dr. K. Fueki for valuable discussions during this work.

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15) Nuclear Engineering Data Sheet No. 15, "Uranium Carbide," *Nucl. Eng.*, **5** (51), 355 (1960).

16) IAEA. Technical Reports Series No. 39, "Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases," p. 3 (1965).

17) R. B. Bird, W. E. Stewart and E. N. Lightfoot, "Transport Phenomena," J. Wiley, New York (1960), p. 504.

*1 Sowden, Hodge, and Moreton-Smith[18] employed gold powder as heat dispersant in their investigation on oxidation of uranium monocarbide powder with oxygen and could eliminate the self-heating effect.

18) R. G. Sowden, N. Hodge and M. J. Moreton-Smith, *Trans. Faraday Soc.*, **60**, 759 (1964).